PROGRESS REPORT #5 BEHAVIOR OF PURE PdD

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INTRODUCTION

Progress reports #1 through #4 can be found at <u>www.LENRexplained.com</u>. This report describes the behavior of a sample of pure Pd that was given a treatment known to improve the reaction with hydrogen. As the result, the Pd achieved a composition of $PdD_{0.98}$, which is near the upper composition limit of the beta phase. A composition this high is rarely produced and according to various theories, is expected to produce excess energy, which is found to be the case. The behavior provides insight into how reaction with deuterium takes place in an electrolytic cell and some of the variables affecting energy production. This understanding can then be applied to the planned study of the Pd-Ag alloys.

RESULT

1. System Upgrades

Previously, the random scatter in measured excess power created an uncertainty of ± 0.05 watt. By inserting a reservoir in the water line before the cooling water reached the calorimeter, this random variation is reduced to about ± 0.02 watt. As a result, the rapid and random variations in cooling water temperature caused by the heater in the constant temperature bath did not reach the calorimeter where the resulting changes in the reference temperature of the thermoelectric convertors (TEC) would cause fluctuations in the Seebeck voltage.

The reference temperature for the TEC was reduced from 20° C to 10° C in order to allow a wider temperature behavior to be explored. The 10,000 mfd capacitor was removed from the voltage circuit of the electrolytic cell because it was apparently not needed.

2. Loading behavior of Pd

The amount of D reacted with the Pd cathode is measured using the orphaned oxygen method. This method measures the amount of O_2 released from the D_2O by electrolysis when the D_2 reacts with the Pd. This oxygen displaces oil from a reservoir onto a balance where it is weighed every 6 minutes. A photograph of the reservoir and balance is shown in Fig. 1. Not only does this method measure the D/Pd ratio, but it also provides assurance that the recombiner is working and no D_2+O_2 is leaving the calorimeter.

The measured composition is calculated from the reaction $2 D_2 O = 4 D + O_2$, which shows that each mole of O_2 will accompany the release of 4 moles of deuterium. This equation is independent of isotopic composition. The moles of O_2 are calculated using the conventional equation PV=nRT, which takes the form below.

Mole deuterium = $[4*(local atmospheric pressure)/760]*[(weight oil)/0.87]*[1/1000]]/{[0.82059*300]}.$

The local atmospheric pressure is near 0.76 atm. A temperature of 300 K is used because the average temperature is frequently near this value. The measured density of the mineral oil is 0.87 g/ml. The number of moles of D released by the applied current is given by the equation

 $D = [(applied current)^*(time, sec)]/96485.$



FIGURE 1. Picture of the oil reservoir and balance used to measure the orphaned oxygen.

Table 1 lists the weight and appearance after the various treatments.

weights and appearance		
Weight of Pd	2.34263	
Weight + stainless lead	2.38537	
Weight after HNO ₃	2.37776	Metallic color
Weight after cooling from	2.37779	Uniform blue color
900°		
Weight after deloading in	2.40858	Uneven brown stain
air		
Weight after deloading at	2.39610	
150°		

 TABLE 1

 Weights and appears

The result of applying 0.102 A to the sample in an electrolyte consisting of D_2O + 0.109 g Li metal is shown in Fig. 2. Several general behaviors are worth noting. First, initially every D+ presented to the cathode by the current reacted. As more D reacts, gradually the efficiency of the electrolytic process is reduced until all D+ presented to the surfaced forms D_2 gas when the composition limit is reached. This gas is reacted with any O_2 present in the cell by the catalyst which returns the D_2 to the electrolyte as D_2O . Consequently, when the Pd stops loading, no net chemical reaction takes place in the cell and the excess power returns to zero. The efficiency of reaction is determined by the purity of the cathode surface.

The power required to cause this reaction is determined by taking the difference between the power measured by the calorimeter, based on a previous calibration, and the amount of power applied as current and voltage.

The electrolytic reaction is endothermic because more power is required to split the D_2O into D_2 and O_2 than is recoverd when the D_2 reacts with the Pd. The shape of the resulting curve is typical of other samples by having a brief time during which excess power is constant followed by a time during which the power increases to zero, generally by following a linear path. The implication of this behavior is examined in the Discussion section.



FIGURE 2. Comparison between average D/Pd ratio and excess applied power as a function of time during the initial reaction with deuterium when 0.102 A is applied at 11°C. Values are measured ever 6 minutes.

The data as displayed at the time of the study is shown in Figure 3. As can be seen in the upper left graph, the temperature of the electrolyte increases when electroytic power is applied but remains slightly reduced while the reaction with D takes place. Once

the sample has reached the composition limit, the temperature increases to a steady value. Consequently, the temperttaure is responding as expected to a reaction that is using energy. The radiation, shown in the center graph, remains relatively constant. The graph on the right shows a gradual increase in the OCV



FIGURE 3. View of computer screen during initial reaction with deuterium.

As will be explained later, the composition of the surface is within the singlephase beta PdD region throughout the reaction and the composition slowly increases as the sample reacts. Consequently, the reaction rate is not controlled by the composition at the surface but by the average composition of the entire sample. This insight is new.

2. Correlation between power production and radiation

Power production by LENR is expected to produce radiation, which has been detected by many studies in the past. However, a clear correlation between radiation flux and excess power has not been reported.

In this study, a large GM detector is placed within 2 cm of the cell wall and the detected radiation is required to pass through about 1 cm of electrolyte and through 1 mm of Pyrex. A photograph of the arrangement is shown as Fig. 3 in Report #1. The surface of the cathode is parallel to the surface of the GM detector. The normal flux in the absence of any radiation generated by the electrolytic cell is about 70 c/m. A similar GM detector is located about 3 meters from the cell outside of the calorimeter and is used to detect changes in background radiation. No changed in background radiation flux is observed during these studies.

Figure 4 shows the relationship between radiation flux and excess power produced when different currents were applied and when the temperature is changed at constant current. The numbers show the sequence for the measurements. When the temperature was reduced after data point #4, the radiation flux returned to its initial value and no excess was produced, as was the case at the start of the study. Consequently, a clear correlation between radiation measued ouside the cell and excess power production is shown.



FIGURE 4. Comparison between excess power and radiation flux for conditions when the excess power is changed by changing the applied current to the cathode and when the temperature is changed while a fixed current of 0.10 A is applied. The numbers show the sequence in which the data are taken.

3. Behavior of OCV

When power is applied to the cathode, the OCV immediately increases from zero to about 1.23 V and then slowly increases as the composition of the bulk increases, as shown in Fig. 5. Values also have been obtained for several fixed compositions. The OCV for PdD_{0.699} is 0.85 V and a OCV of 0.56 V is measured for PdD_{0.416}, a composition containing both the alpha+beta phases. The value can be assigned to a composition of PdD_{0.60}, which is the composition of the beta phase in equalibrium with the alpha phase under the conditions of the study. These values can be used to calculate the composition at the surface in future reports. As shown in Report #4, the OCV is decreased by increased temperature.



FIGURE 5. OCV vs time during initial reaction with deuterium.

4. Effect of temperature on power production

Past studies have shown that a critical current must be applied to the cathode to initiate excess power production after which additional current causes the excess power to increase. This effect is attributed to the current causing the composition in the surface region to increase, thereby causing the rate of energy production to increase. However, the temperature of the cathode surface is also changed by this applied current. The role of this temperature change has not been considered in the past. The apparatus used here is designed to allow the temperature of the cathode to be changed independently of the change caused by applied current. While current is applied to the cathode by one power supply, another power supply can supply current to a resistor located within the cell, thereby changing the temperature of the cathode. The circuit and its calibration are described in Report #2.

Two conditions were explored and compared in Fig. 6. In one case, the cell temperature is changed by changing the amount current applied to the electrolytic process. In the other case, the current used to cause electrolysis is fixed at 0.1 A, which does not produce excess power. In the the case, temperature is increassed by applying power to the internal resistor. The good agreement between these two studies shows that the temperature of the cathode is the main variable affecting power productiion, not applied current. No excess power is detected below a temperature of 35° C. The slight negative value for excess power are not real but the result of a slight error in the calibration at small values of the Seebeck voltage perhaps caused by changes in room temperature. The average scatter of the 16 values on which the calibration is based is ± 0.013 watts.

The sample had an average D/Pd ratio near 0.7 during these measurements. Apparently, a high D/Pd is not requited to make some excess power once the sample becomes nuclear-active.



FIGURE 6. Comparison between applied power produced by using a variable applied current or a fixed applied current of 0.1 A while causing a change in cell temperature. The amount of applied current is shown.

5. Excess volume and other behaviors.

As discussed in Report #4, palladium changes shape in ways that produce extra volume in the bulk material. The larger the amount of excess volume, the less likely high loading can be achieved and excess energy will result. The sample studied here is unusual in that it produced only a small excess volume, deloads very slowly even at 150° C, and shows only minor changes in the surface features after loading and deloading. The surface of the orginal Pd is shown in Fig. 7 along with the composition using EDX with 20 keV electrons. Only C and O are detected on the surface as unpurities. After the study, the surface shown in Fig 8 is essentially unchanged, but various impurities are clearly visible both in the EDX spectrum and seen as color changes using optical light. These deposited impurities significantly reduce the rate at which D reacts when the sample is again electrolyzed. If cracks are present, their width is less than 1 micron.



FIGURE 7. SEM view of the initial surface and its composition.



FIGURE 8. SEM view of the surface after the study and the surface composition using EDX. The Fe and Cr probably resulted from the stainless steel wire used to attach the sample in the calorimeter.

6. Future studies

Application of laser light is known to increase the amount of power and a change in the wave length of the light is known to cause a change in how the laser light affect heat production. This behavior is not understood, but nevertheless is used to support several theories. The apparatus is designed to explore this effect while testing the role of many variables not explored in the past. Figure 9 shows the location of the laser relative to the calorimeter. The inherent accuracy of this calorimeter allows much uncertainty in previous stiudies to be eliminated. This study will start when samples having a reliable production of excess power are available.



FIGURE 9. Overall view of the calorimeter showing the position of a laser. A laser is positioned to apply laser light to the cathode surface at various angles and locations. The laser can be focused to change the spot size on the target, heated to change its frequency, and rotated to change its polarization relative to the target. A second laser can also be used either together or independently. A hole through the back of the calorimeter allows insertion of a fiber optical cable to measure the frequency of the laser. The laser is not being used at the present time.

DISCUSSION

1. Loading behavior

Most samples of palladium are not able to load to the high value achieved by this sample. Consequently, this rare event provides an opportunity to study some of the behaviors this project was designed to explore using the Pd-Ag alloy rather than pure Pd.

A sample able to load to such a high average deuterium content demonstrates the presence of certain important physical characteristics. These are the absence of large cracks and the ability of the surface to react easily with deuterium. These characteristics are important because large cracks allow escape of the deuterium after it has entered the structure, which reduces the ability of the nuclear-active surface region to retain

deuterium. Also, creation of large cracks prevents creation of the nano-cracks I propose are the nuclear active environment (NAE). So, from my viewpoint, the ABILITY to reach a high composition is an important fact because this shows the sample is not flawed. This ability alone does not create the NAE, but is only an indication of the potential ability to form the required NAE. Other tests are also available.

Once the NAE forms, the average composition, as well as other variables, influence the amount of power produced by the sample. Of these variables, my theory identifies temperature at the NAE as being a major variable affecting power production because it determines how fast deuterium, the fuel, can reach the NAE by diffusion. In short, the temperature is the throttle for the process. Consequently, the apparatus is unique by allowing this variable to be easily explored.

2. Calculation of the energy/mole deuterium to form PdD_x

Let's start by analyzing the loading behavior shown in Fig. 2. As the Pd reacts with D, the energy being used to cause the reaction remains constant up to 230 minutes, at which time the average composition, shown by the red line, has reached a value at which the alpha phase is no longer present in the material. This conclusion is based on the data(1) shown in Fig. 10 where the D/Pd ratio vs equilibrium pressure is shown for 11°C, the temperature of the Pd during loading. The presence of two phases during this time forces the chemical properties to have a constant value, hence the power being used remains constant. In other words, in this region, the alpha phase is being converted to the beta phase remains, the amount of energy being used slowly decreases. This decrease is caused by a combination of less D being added to the PdD each second and because the energy released by this reaction changes. This behavior is typical of all samples of Pd studied. Other examples can be seen in Figs. 87 and 89 in my book.(2)

The rate at which D is added to the PdD and the excess power being applied can be combined to calculate the energy/mol deuterium being reacted. This calculation is done as follows: The orphaned oxygen method measures the amount of deuterium that reacts with the Pd every 6 minutes. The measured power used during that time is multiplied by the number of seconds to determine the number of Joules used during the 6 minutes. The power is divided by the number of moles of D to obtain the energy/mol D used during each time interval. This value is plotted in Fig. 11. The energy/mol D being used to decompose the D₂O is also shown. As long as the measured values are less negative than the values for D₂O, formation of PdD is adding energy to the reaction.



FIGURE 10. Relationship between D/Pd ratio and equilibrium pressure of D_2 at 11°C¹. The relationship shows that alpha phase forms in equilibrium with $PdD_{0.60}$ and the sample contains two phases at average compositions less than D/Pd=0.60. (from Santandrea and Behrens (1))



FIGURE 11. Enthalpy for the reaction $Pd + 0.5D_2O = PdD + 0.5O_2$ at 11° C. The negative sign indicates that energy is added to cause the reaction. The line indicates the amount of energy required to decompose 0.5 mole of D₂O. The x-axis is the composition into which 1 mole of D is added.

¹ The relationship indicates the equilibrium pressure of D_2 over $PdD_{0.98}$ is near but less than $4x10^7$ atm. This pressure DOES NOT exist in the lattice itself as some theories propose. This is the equilibrium pressure of the gas phase in contact with the solid beta phase. This high effective pressure or activity is achieved using electrolysis without an actual gas phase being present at the reaction site. The observed gas has a pressure shown in Fig. 2 and this can achieve a composition only near PdD_{0.68}.

Consequently, the calorimeter would measure less energy for the reaction than is required to decompose D_2O . Apparently, at the low composition boundary of the beta phase, formation of PdD adds very little energy. As the composition is increased, the amount of energy added/mol D increases slightly until a composition near PdD_{0.95} is reached. Compositions greater than this value require energy to form so that the over all reaction requires more energy than is needed to decompose D_2O . This behavior is inherent in the shapes of the two curves plotted in Fig. 2, which is typical of all electrolytic reactions involving D_2O and Pd. This extra energy that is required to form compositions above PdD_{0.95} shows why compositions greater than this are so rarely formed and would imply that the equilibrium pressure of D_2 increases sharply at compositions above this value. This is a new conclusion.

This behavior can be compared to the measurements reported by Sakamoto et al.(3). This measurement obtained the relationship $\Delta H(D)$ (kJ/mol) = 44.99 - 41.89 D/Pd, which predicts a reduction in the energy/mole deuteron as the upper limit of the PdD phase is approached. In contrast, this work shows an increase in the energy/mole deuterium until a composition near PdD_{0.9} is reached, after which the PdD compound becomes less stable with respect to its elemental components. The implications of this observation will be discussed in a future paper.

3. Correlation between radiation and excess power

Although the measured radiation flux is small, it correlates with the amount of power produced. The detected radiation is expected to be a small fraction of that being generated at the cathode and would consist mainly of the high-energy tail. Having samples able to generate more excess power will make possible measurement of the energy. Now that radiation can be detected, use of cells having a thin window is encouraged in order to increase the amount detected. This study will be continued in the future.

4. Effect of temperature on the amount of power produced.

The previous interpretation of how applied current affects power production is wrong. The important variable is actually the temperature change caused by the applied current. The composition at the surface produced by the current is apparently not important. Instead, small changes in temperature determine how much power can be produced by the nuclear reaction, which is an amazing realization. Now theory must explain how this effect is possible. Consequently, this behavior has important implications to the creation of an explanation for the LENR process. At the very least any theory proposing to cause LENR at low temperature can be rejected.

Now that temperature is found to be the important variable for creating excess energy, use of high-applied current in future studies is no longer required. Several advantages become apparent. Use of a low-applied current will reduce the amount of impurity deposited on the surface and the tendency for the cell to explode when the recombiner fails will be reduced.

SUMMARY

A method is used to load Pd to $PdD_{0.98}$. This material made excess energy while the composition is near $PdD_{0.7}$.

The excess energy is correlated with production of radiation detected outside the cell. Future measurement of the radiation energy will give insights into the mechanism from which it results.

The temperature of the cathode is found to be the major variable in producing excess energy, not applied current.

The loading behavior is used to calculate the enthalpy of formation of PdD as a function of composition. Compositions above about $PdD_{0.95}$ require energy for their formation.

The OCV was measured and can be used to calculate the surface composition. Application of these observations to theory will be undertaken in future Reports.

REFERENCES

- 1. R. P. Santandrea, R. G. Behrens, A review of the thermodynamics and phase relationships in the palladium- hydrogen, palladium-deuterium and palladium-tritium systems. *High Temperature Materials and Processes* **7**, 149 (1986).
- 2. E. K. Storms, *The science of low energy nuclear reaction*. (World Scientific, Singapore, 2007), pp. 312 pages.
- Y. Sakamoto, M. Imoto, K. Takai, T. Yanaru, Calorimetric enthalpies in the b-phase regions of Pd black-H(D) systems, in Sixth International Conference on Cold Fusion, Progress in New Hydrogen Energy, Ed: M. Okamoto, (New Energy and Industrial Technology Development Organization, Tokyo Institute of Technology, Tokyo, Japan, Lake Toya, Hokkaido, Japan, 1996), vol. 1, 162.